Insulating Biomaterials
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Introduction

This report will focus mainly on results of long term soak results of surface encapsulants on silicone dioxide. Instrumentation for silicone adhesion testing has been implemented and example pull tests have been accomplished. PPECVD silicone coatings for wire insulation have been under development and some recent results of that work will be presented. Pass Chip results from the last fabrication run will be reviewed and the lithium battery soak tests results will be summarized.

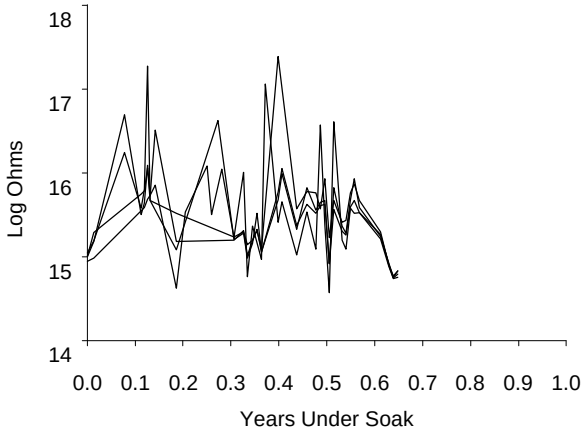

Figure 1: Open circuit test of 384 channel electrometer system.

Instrumentation

The 384 channel electrometer system has been working well taking continuous data. An example of an open circuit channel measurement which includes a 3 foot long Teflon insulated 12 wire cable used to connect old jar type samples is shown in Figure 1. The curves are somewhat jagged primarily due to the fact that data is taken twice per week. The noise of the new system is comparable to the old system in fact. The data should be taken every 2 days but the current computer running this system is too slow to compile the data any faster than once per week or so. A new computer will be implemented next quarter to speed these measurements. As more data is taken, and more rapidly, the large number of data points can then be averaged to smooth the noise further. Thus it is expected that resistances up to about $10^{15}\Omega$ can be measured consistently with this system.

Silicone Encapsulation Long Term Testing - 37°C Saline Soak

Some of the long term encapsulation results are included here. Recently, programming was written to extract data from the several different files generated by the several different test systems encountered by these long term survivors. Figure 2 shows summarized results from the first successful bond chip test. The encapsulation material was Dow Corning MDX-4-4210. Recall that bond chips have concentric rings of interdigitated electrodes. There are 5 pairs of electrodes in each ring, with 10μm platinum traces separated by 20μm spaces. Adjacent sets of electrodes are spaced 20μm apart. Bonds are made in the center of the concentric arrays. The outer traces

are within about 100μm of the edge of the chip. These resistance measurements should be multiplied by approximately 4,000 to convert to ohms/square.

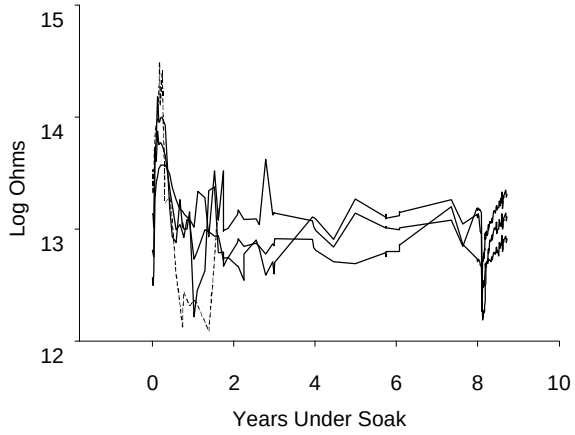

Figure 2: Dow Corning MDX-4-4210 sample on a silicon dioxide bond chip with platinum metallization. The device associated with the dashed trace failed after about 18 months.

For the example shown in Figure 1, the inner trace set failed. This could have been for several reasons, but the most likely is that there was subtle contamination from the bonding process that shedded particulates on the inner traces that eventually created a conducting path. In spite of what must now be a fairly intense electrochemical environment within the failed traces, the adjacent traces have remained intact for an additional 7 years.

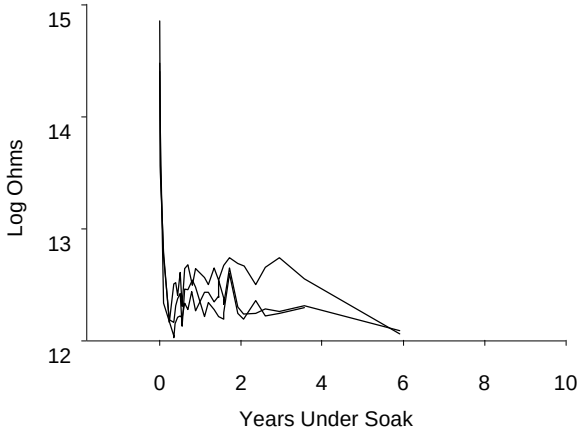

Figure 3: Carbon filled experimental silicone from Dow Corning (x6863C) on bond chip.

By the 6th year measurements were becoming infrequent due to the number of devices under soak testing and a new system was developed that would allow continuous testing. During year 8, this test device was placed under continuous measurement in the new system. This particular sample underwent a transient change in readings shortly after being installed in the new system. There may have been condensation on

the outer connector of the test jar which provided a $3x10^{12}\Omega$ shunt. Since the initial transient, readings have been normal for these three devices. This is a typical result for silicone elastomers currently under test.

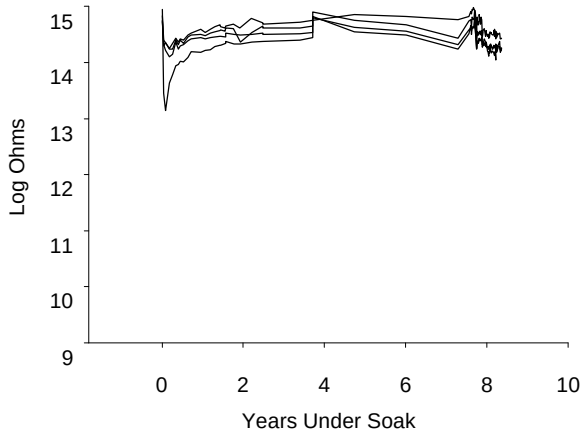

Figure 4: Dow Corning x6863B without carbon on bond chip.

Figure 3 shows results from a carbon filled experimental silicone (x6863C) obtained from Dow Corning electronics products division. This material is not available commercially. However, initial readings were very high until soak testing began. Then devices began to fail after about 6 months. 3 devices survived over 3 years, but all have failed after 6 years. While this result could have been due to inadvertent surface contamination of the sample or failure of the bulk properties of the material, it is more likely due to the carbon filler which provides isolated conducting paths throughout the material and particularly at the silicon dioxide interface.

Figure 4 shows long term soak results of a bond chip protected with x6863B without the carbon filler. This is a much better behaved sample where all four electrode sets have maintained high resistance readings for over 8 years. This plot shows perhaps some curvature but the readings between years 3 and 7 were too infrequent to have confidence in identifying a weak trend. However, data since 7.5 years has been taken on a weekly basis with the new electrometer system.

Figure 5 shows results from a bond chip with a similar material to x6863B but without and adhesion promoter (x8069). Contrary to expectations, this material maintained a higher resistivity than the x6863 from the beginning and is continuing to demonstrate extraordinarily high resistance readings that are at the upper limit of the range of the new electrometer system. One electrode set failed after about 2.5 years. This set was the second from the inner electrode set. In spite of this failure, the electrode sets on either side of the failed set continue to maintain very high resistance readings.

We have many other examples of silicones, mostly successful, that may be useful for encapsulation of silicon dioxide surfaces. The only silicone materials that have consistently failed our testing were resin filled systems. Resin fillers are used where optical clarity is important (artificial lenses). Mechanical tests of these materials showed rapid degradation of Young's modulus indicating that the structure of the film

had been weakened. This may be due to hydrolysis of weak resin-elastomer bonds. Precisely why this might be related to failure of the surface adhesion is not fully understood but may be due to evolution of micro-voids around the filler particles which somehow coalesce on the surface of the silicon.

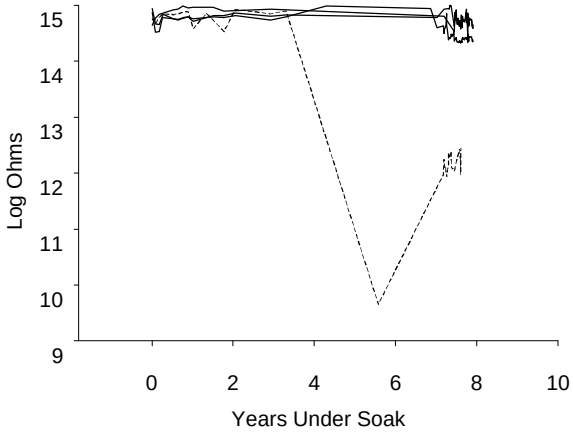

Figure 5: Dow Corning x8069 experimental silicone on bond chip. Dashed line is failed electrode pair (second pair from inside bond pads).

Silicone Encapsulation Long Term Testing - 90°C Saline Soak

To accelerate the aging process, up to 128 devices assembled into long tubes can be tested in the high temperature soak system at 90°C. There are also slots for 128 samples to be tested at 80°C, but this has just recently been implemented. It must be kept in mind that accelerated testing is far more an art than the Arrhenius plots would indicate. There are many pitfalls in using heat to accelerate the aging process. One is that the chemical reaction is assumed to be first order. It is necessary to determine the activation energy for the process. There must be no "gettering" processes ongoing, and there cannot be competing reactions with different activation energies that could differentially accelerate thereby changing the nature of the system at different temperatures. Thermal expansion issues should not dominate the results. I am sure there are other issues as well, but this list is intended to inject caution to the interpretation of the high temperature soak data.

The high temperature soak tests use long tubes in hot blocks where only the bottom of the tubes are heated. Triple track devices were developed to allow testing of the surface properties of the encapsulants without the confounding problem of particulates falling onto the test areas during bonding as was the case for bond chips. These devices have a single current emitting trace surrounded by two current sensing traces. Only one test device is included on each substrate, and four substrates are assembled into each test tube assembly.

There is greater noise for measurements taken at 80°C and 90°C than for room temperature measurements. This is thought to be due to charge re-distribution events caused by droplets of condensed water running or falling down the tubes during measurements.

Figure 6 shows results from long term testing of MED4-4220 from Nusil on a triple track device. One of the devices failed after a few months while the remaining devices apparently have failed after 1 year though this must be verified. About this device was assembled we had recently changed laboratories and were in the process of re-establishing assembly procedures which may in some way account for the failure as well. Other samples of MED4-4220 are under soak to verify this result.

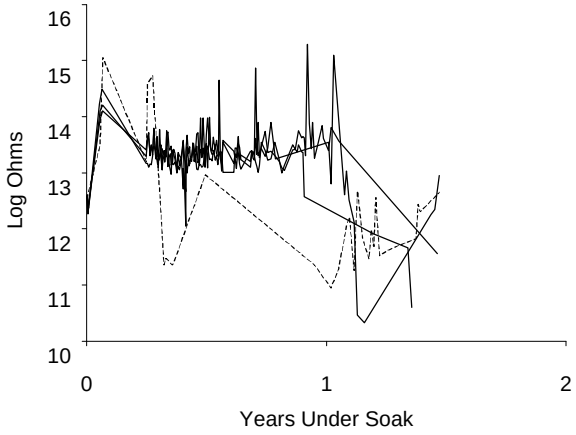

Figure 6: 90°C saline soak test of Nusil MED4-4220 on triple track devices.

Figure 7 shows results of long term soak tests of triple tracks coated with Huls PEM25. This material is also similar to the Dow Corning MDX-4-4210 and has been performing well for over 3 years with the exception of 1 device.

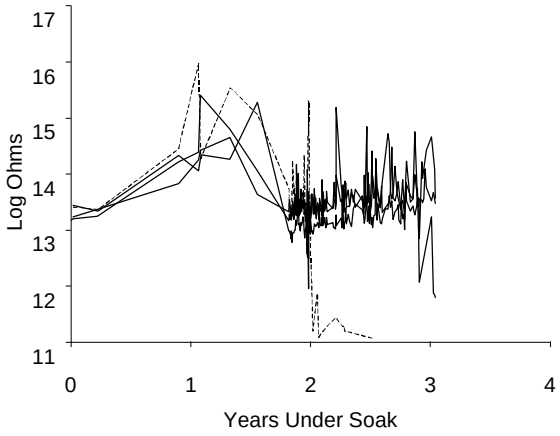

Figure 7: 90°C saline soak test of Huls PEM25 on triple track devices.

Figure 8 summarizes testing of CV2500 coated triple track devices. CV2500 is a Nusil product similar to MDX-4-4210 that is ultra-purified before delivery. All four devices have been performing well at 90°C for over 2 years, but there is no apparent difference between this material and the other MDX-4-4210 analogs for this application.

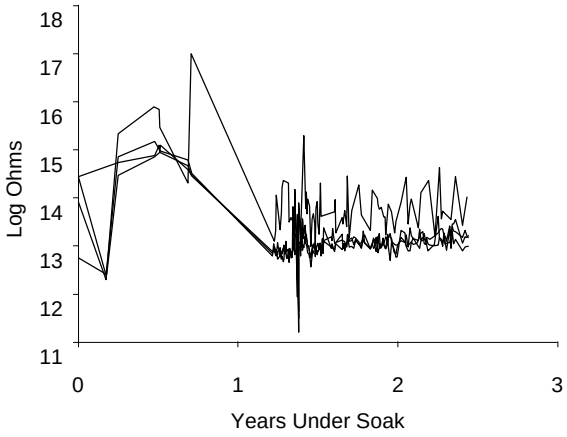

Figure 8: 90°C saline soak test of Nusil CV2500 on triple track devices.

Other silicones are also under test but the general finding thus far is that all of the MDX-4-4210 like materials appear to perform well as encapsulation for the silicon dioxide surface. Differences in the materials are minor in that cure times, viscosity, durometer all can vary somewhat, but such differences do not have a significant effect on the long term performance.

Silicone Adhesion Testing

The pull test apparatus was modified to allow pull testing of materials from substrates to evaluate mechanical adhesion. The purpose of these experiments is to clarify the value of various cleaning steps used to prepare silicon dioxide surfaces for application of silicone encapsulants. While we have had good success with silicones for protection of silicone dioxide surfaces, some devices fail unexpectedly. These failures may be related to the state of the surface prior to application of the silicone under test.

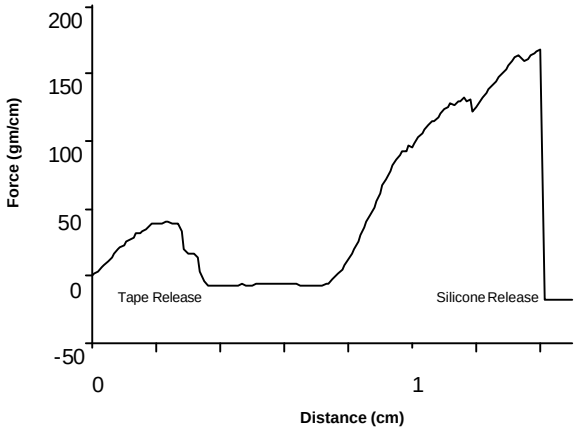

Figure 9: Silicone peel test example on uncleaned silicon chip using fully cured Nusil CF20-2186. The tape release bump is an artifact caused by a small portion of the Kapton tape being stuck to the silicon at the beginning of the pull.

Samples are prepared by first cleaning 1cm silicon squares using some portion or all of the established cleaning protocol. Next the silicone under test is applied and a piece of

Kapton tape is embedded in the silicone to provide a handle for pulling on the silicone-silicon dioxide interface. The sample is cured (which is also a variable to be evaluated). The sample is trimmed to provide a 5mm wide strip to be peeled. It is then peeled off orthogonal to the substrate in the micro-pull test apparatus. By using a long piece of tape for pulling, the angle of the force relative to the substrate can be maintained close to 90° throughout the peel. An example test was run as an example and the resulting force plot is shown in Figure 9. More experience with this test is needed before a series of samples will be prepared under differing conditions and evaluated. One issue with the result shown in Figure 9 is that after the silicone begins to release from the substrate, the force should remain constant until total delamination. This is observed to some extent but there is still a substantial increase in force until total delamination. Probably the film was peeled too rapidly.

Once the instrumentation and technique are fully developed, a variety of samples will be prepared with different surface cleaning protocols, and cure schedules to identify the critical points in silicone encapsulation methodology. This information will allow us to prepare more consistent samples, and will improve the odds that other laboratories will be able to duplicate our results using silicone encapsulants.

PPECVD Fluorocarbon Depositions

The PPECVD fluoropolymer research has not been abandoned though the focus of current research is on PPECVD silicones which is a competing solution to the problem of surface insulation of wires and silicon devices. The fluoropolymer material developed during Scott Limb's thesis work has all the characteristics of PTFE Teflon except for temperature stability. The PPECVD material would need to have this parameter fine tuned to be of use for implantable devices, but we ran out of time as Scott graduated. Still we thought we had enough data and understood the film well enough for now. Figure 10 summarizes results from one set of fluoropolymer surface coating tests. The test device consists of a silicone coated silicon square with an o-ring exposed area that was coated with the fluoropolymer film.

One of the many devices we tried to test on silicon surfaces is actually still under soak and apparently doing well while the others failed after about 4 months due to delamination of the films. Wire tests were difficult to accomplish partly because of the fragile characteristic of the film which goes along with the high temperature instability. Notably, if the film were more cross linked it would be tougher and have higher thermal stability, but we were focussed on flexibility for most of the work which goes in the opposite direction. The current test result summary is shown below. Note that a crack in the jar cap occurred which compromised the data for a time, and may have led to failure of three of the devices. The cap has now been fixed and testing is continuing.

When we began with a new graduate student we reviewed the fluoropolymer data and decided that considerable effort would be required to bring this along as a clinical material. In view of success we had in developing the fluoropolymer film, we felt it would be worthwhile to instead focus on the silicone coatings. If successful, it would be nearly universal and would afford the possibility of a single, continuous

encapsulation about the entire device that might fully protect the surface as well as the wires and integrated circuits.

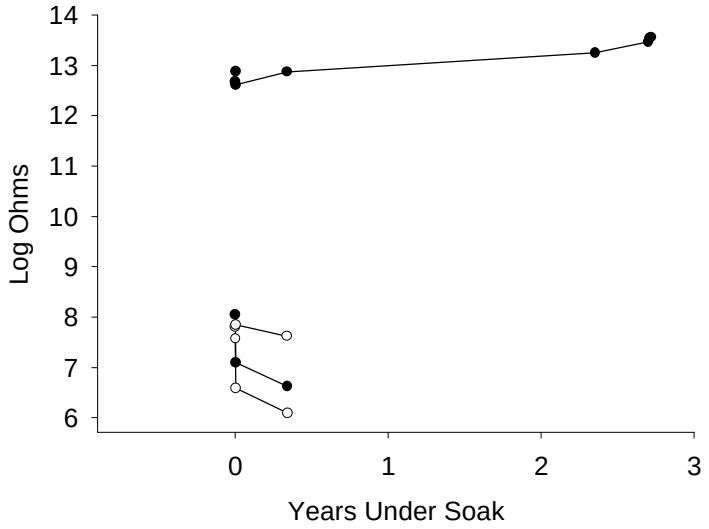

Figure 10: 90°C saline soak test results of fluoropolymer coated silicon surfaces. Test devices consisted of o-ring exposed flat surface coated with material under test.

Pilot experiments showed that by following an analogous path to the fluoropolymer development we could indeed control the properties of silicones in ways that others had not been able to achieve. The material sticks well to silicon substrates which makes it easy to test. More importantly, early experimentation showed that the thermal instability issue with the fluoropolymer coatings was not an issue with PPECVD silicone coatings.

At that time, there was also considerable commercial interest in the fluoropolymer coating so the decision to focus our resources on the silicones for some interval did not really detract from further development of the fluoropolymers in parallel. Thus we plunged into silicone development and have now begun producing films that show more promise than the fluoropolymers for protecting substrates and wires alike. They are much tougher, thermally stable films. Also, they do not exhibit etching of platinum wire as the fluoropolymers did. Now we feel we are far advanced with the silicone films though they are not as well characterized as the fluoropolymer films. For example, we have over 40 silicone samples under test but only 1 fluoropolymer film under test. The reason is that the silicone films are inherently easier to handle and exhibit fewer defects though particle contamination is still a problem.

PPECVD Silicone Depositions

Development of silicone depositions from plasma sources continued. The relatively large experimental parameter space involving starting monomer, pressure, flow, argon fill, and pulse conditions were explored further to further refine boundaries of useable conditions. The main criteria were that the depositions should not crack on or peel from silicon dioxide surfaces, should form a conformal coating about suspended wires, should be durable to handling and should be flexible enough to allow bending of wires.

Wire bending flexibility was tested initially by tying the wires in 800μm diameter knots and observing for fracture of the film from the wires. This was revised to observing fractures following wrapping of the wires around 800μm diameter posts because it was apparent that friction was causing breakage of the films during the knot tying.

Many of the films on silicon chips that were under soak last quarter remained viable and are continuing testing. 32 new samples were fabricated and will be placed under soak next quarter for long term evaluation. Since these films are as thin as 0.7μm, leakage currents are a little high for this measurement system, but can still be accomplished. Next quarter, one bank of electrometers will be modified to have reduced sensitivity which will allow more accurate measurement and tracking of these devices as they age.

Film flexibility was monitored by wrapping coated 3 mil wires around an 800μm diameter post and observing fracture of the film. Examples from a series of wire coatings under various deposition conditions are shown in Figure 11, Figure 12, and Figure 13. Some of the tradeoffs include flexibility, abrasion resistance, tensile strength, growth rate, and electrical resistivity. In this series, it is clear that for our purposes the 100/600 on/off cycle under these chamber conditions resulted in the better film of the three. While additional work must be accomplished to properly identify the best set of conditions, the 100/600 cycle is currently producing satisfactory results that can be further tested on real structures next quarter.

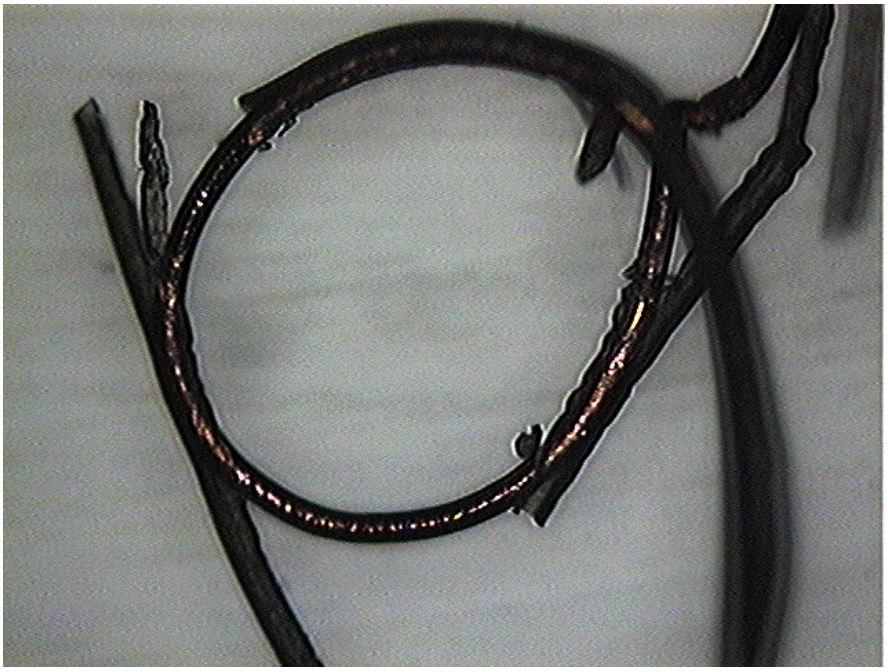

Figure 11: PECVD silicone deposited from D3 monomer for 50 minutes under continuous plasma conditions. Loop was formed about an 800μm diameter mandrel.

A new chamber is being designed to improve gas transport, substrate temperature control, and gas dispersion. Also, a side port opening chamber will be used to improve particulate control.

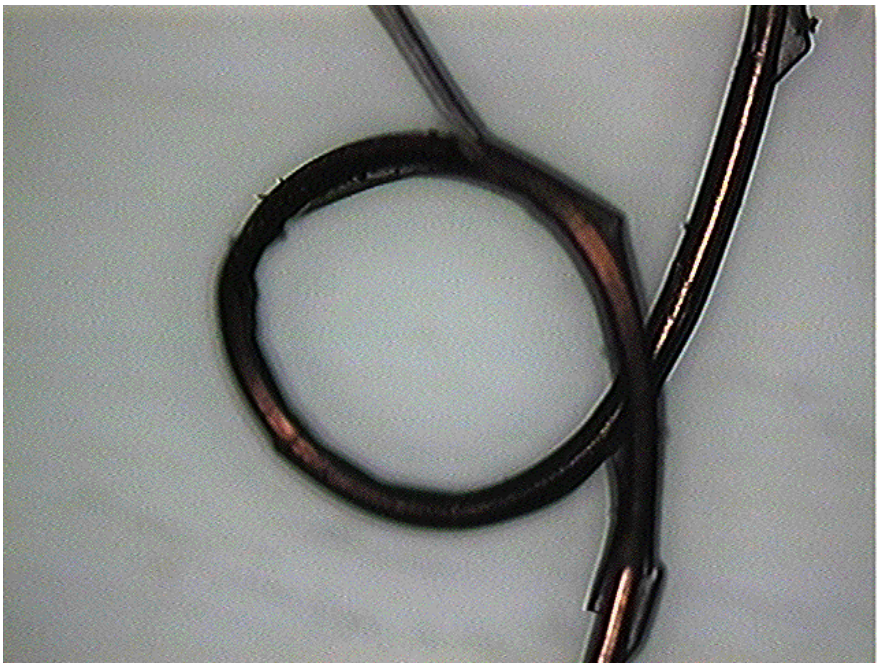

Figure 12: PPECVD silicone deposited from D3 monomer for 50 minutes using pulsed plasma conditions with a 10-on/60-off cycle. Loop was formed about an 800μm diameter mandrel.

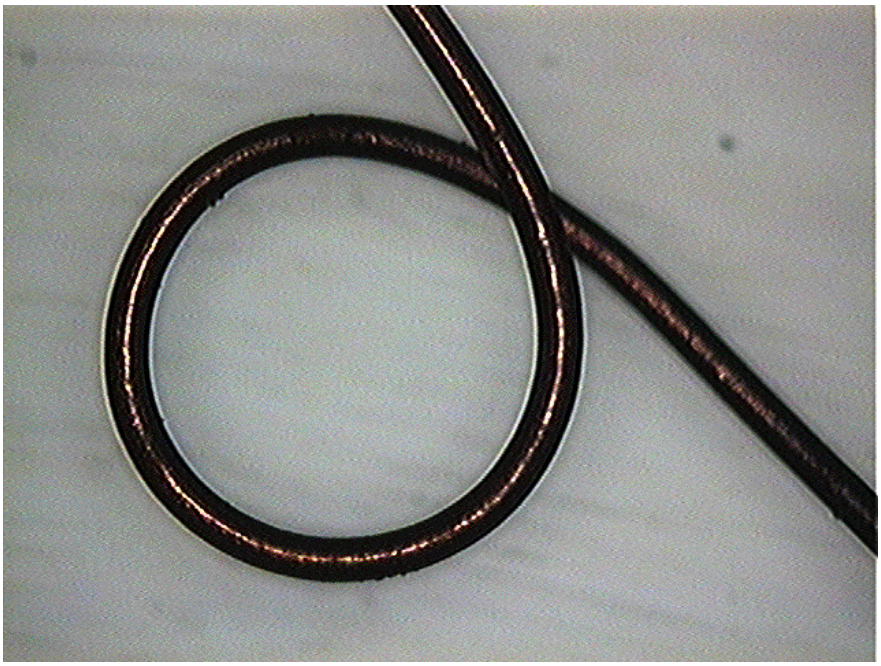

Figure 13: PPECVD silicone deposited from D3 monomer for 50 minutes using pulsed plasma conditions with a 100-on /600-off cycle. Loop was formed about an 800μm diameter mandrel. Note absence of cracking.

Integrated Circuit Test Chips

The integrated circuit test chips were received from MOSIS and evaluated. A proportional to absolute temperature current source reference functioned as designed providing reference currents of approximately10nA and 50nA. The multiplexer system and transmitter also worked as designed. The charge integrators worked well but a design error in the reset circuitry required that they be manually reset for bench testing. The error occurred when the range of the integrators was increased to provide greater dynamic range. However, body effect of the n-channel transistors was not properly taken into account. Subsequently the reset threshold was greater than could be reached by the integrator. Because of this flaw, the devices were not suitable for actual measurement use. An improved reset circuit for the charge integrators was designed and a more thorough test chip with more subunits was prepared. Devices are expected in December of this year.

The LED to be used to transmit information from the passchip has survived continuous saline soak for over 3 years so far, and the prototype optical transmitter system implanted over 2 years ago in a rabbit (VA19) is still functioning as well.

Lithium batteries (Tadiran) to be used for powering these devices were encapsulated in silicone and placed under open circuit saline soak about 18 months ago. Figure 14 shows theoretical 4μA discharge curve. Also shown are measured data from the open circuited batteries under soak indicating that so far the leakage current in the batteries is probably less than 4μA. Magnification aided visual inspection of the battery seams, seals, and glass feedthroughs did not reveal any evidence of corrosion. Additional batteries were procured and a second set will be evaluated with 1MegOhm loads and 100kOhm loads to experimentally determine the 3.6μA and 36μA discharge characteristics.

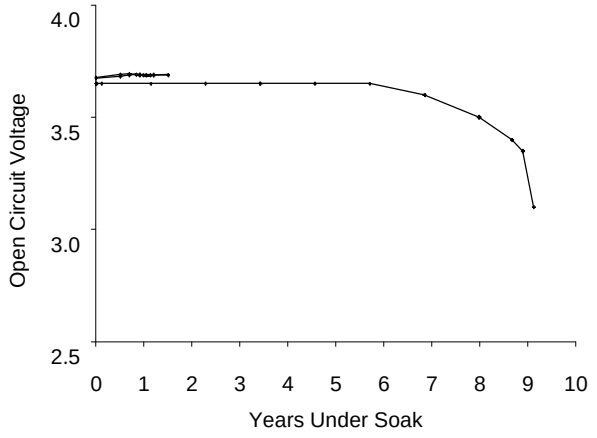

Figure 14: Manufacturer's 4μA load discharge curve and experimental open circuit measured voltages for Tadiran Lithium Batteries to be used for powering PassChips.

These battery soak tests are consistent with the possibility of using silicone encapsulated lithium batteries for long term powering of the PassChip system when available.

Next Quarter:
Compilation and interpretation of data will be the primary focus along with continuing the measurements of all devices under soak or implanted. A series of adhesion tests will be conducted for the silicone-silicon dioxide system as a function of cleaning procedures. Various implantable triple track devices and functional neural probe assemblies, and silicon surface testers will be coated with PPECVD silicone, soak tested and then implanted in animals if warranted. The PassChip will be characterized and put under soak tests if functional, or the design corrected and improved and re-submitted for fabrication. Additional triple track devices for the 80°C soak system will be fabricated and placed under test as well.